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**(54) BUILD-UP SUPPRESSOR AGENTS, COMPOSITIONS CONTAINING THEM AND METHOD OF
USE IN POLYMERIZATION PROCESSES**

MITTEL ZUR VERHINDERUNG VON BELAGBILDUNG, ZUSAMMENSETZUNGEN DIESE
ENTHALTEND, UND ANWENDUNGSVERFAHREN FÜR POLYMERISATIONSPROZESSE

AGENTS SUPPRESSEURS D'ACCUMULATION, COMPOSITIONS A BASE DE CES AGENTS ET
PROCEDE D'UTILISATION DANS DES PROCEDES DE POLYMERISATION

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Description

[0001] The present invention relates to build-up suppressor agents and compositions containing such suppressor agents, which are capable of inhibiting the formation of build-up in vinyl acetate or vinyl chloride polymerization processes, or in polymerization processes utilizing a mixture thereof, with or without other vinyl monomers polymerizable therewith, which processes are effected in aqueous suspension, aqueous emulsion or in bulk.

[0002] In all the above polymerization processes, part of the formed polymer tenaciously adheres to the reactor walls, thus forming so-called "build-up" (otherwise said "scale"), with deleterious effects toward both the final product itself, due to small fragments of build-up which, by detaching from the reactor walls, can be included in the polymerized product and the safety of the reaction because the build-up slows the thermal exchange of the wall giving rise to safety problems due to overheating.

[0003] This build-up is a drawback for the polymerization operations since it is necessary to clean the walls after each repeated reaction.

[0004] This cleaning is costly as it decreases the plant output and is dangerous for the operators due to the toxicity of the monomers, particularly vinyl chloride.

[0005] A number of products and techniques have been developed to mitigate this problem, all of which are based on coating the reactor walls with products which should inhibit adhesion of the build-up or even its formation, as an example by preventing the polymerization of the monomers on the reactor walls. Phenol-formaldehyde condensation products (GB 1439339; JP 54-107991; CA 1181899; EP 0052421) or dye mixtures (alizarin, xanthones, natural flavonoids, naphthoquinones, hydroxyanthraquinones and others) with film-forming elements such as polysaccharides, polyvinyl alcohols, polyvinylpyrrolidone were proposed as reactor wall coating. See for example patents JP 04342701; JP 04154804; JP 04154801; JP 04154805; JP 04108805; JP 04159302 and JP 04031402.

[0006] EP 0 614 915 suggests the use of condensation product between quinones and heterocyclic compounds having at least two amino groups, whereas in EP 0 606 013 there are described, among others, condensation products between quinones and particular diamino-diphenyls substituted with carboxylic or sulfonic groups. Finally, in EP 0 695 761, it is described the use of products obtained by condensing a "phenol" compound, such as, for example, phenol or 1-naphthol, in the presence of an aliphatic dicarboxylic acid.

[0007] The products more widely used seem to be those described in EP 0 052 421. However, although remarkable results as to suppression of build-up formation are achieved, those agents do not allow carrying out an appreciable number of repeated polymerizations.

[0008] All these build-up suppressor agents can be applied in a number of manners, which depend on the nature of the product and on their capacity of adhering to the reactor walls.

[0009] The more common methods provide coating by painting or spraying, in which case it shall be necessary to prepare suitable solutions of the same products, for example aqueous solutions. In case of spraying, nitrogen or water vapour at 5-15 bar pressures can be used as propellant.

[0010] As said above, the performances of these products can be enhanced with the use of film-forming agents such as, for example, polysaccharides or highly hydrolyzed polyvinyl alcohols.

[0011] It has now been found, and this is an object of the present invention, that build-up suppressor agents particularly effective in polymerization processes of vinyl chloride or of vinyl acetate, or of mixtures thereof, in the presence or in absence of other monomers or polymers polymerizable with them, comprise condensation products among an aldehyde (A), a phenol compound (B) and an aromatic carboxylic acid hydroxy-substituted on the aromatic nucleus (C). These agents, as such or in the form of compositions suitable for coating, have demonstrated to be capable of suppressing in a practically complete manner, the build-up formation on the inner reactor walls and, in general, of reaction systems, also when applied in amount definitely lower than those normally used, as well as to allow the carrying out of repeated polymerizations without having to apply, each time, the agents before each run and without noticing significant variations of build-up formation between the first and the last reaction.

[0012] These agents are endowed with another favourable characteristic, i.e. they have a reduced sensitivity with respect to pH variations in polymerization processes, and possess a remarkable shelf-life.

[0013] Moreover, the polymers obtained show better physical characteristics.

[0014] Therefore, a further object of the present invention comprises compositions containing one or more of the above build-up suppressor agents.

[0015] Another object of the present invention is the use of one or more of the above build-up suppressor agents in polymerization processes of vinyl chloride or of vinyl acetate, or of their mixtures, in presence or in absence of other monomers or polymers polymerizable with them.

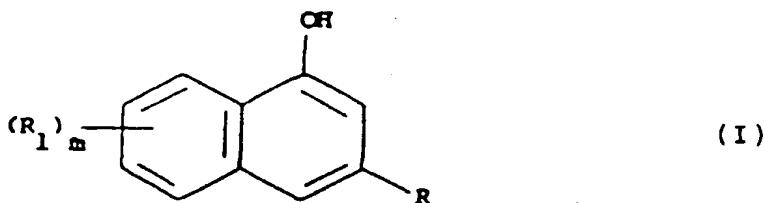
[0016] Still another object of the present invention is a method for suppressing build-up formation in polymerization processes of vinyl chloride or of vinyl acetate, or of their mixtures, in presence or in absence of other monomers or polymers polymerizable with them, which comprises coating the inner walls of a polymerization reactor with one or more of the above build-up suppressor agents.

[0017] The present invention further comprises a polymerization process of vinyl chloride or vinyl acetate, or their mixtures, in the presence or in absence of other monomers or polymers polymerizable with them, effected in a reactor whose inner walls are coated with one or more of the above build-up suppressor agents, and the polymers obtained by means of said process.

5 [0018] Finally, a further object of the present invention is a polymerization reactor whose inner walls are coated with one or more of the above build-up suppressor agents.

[0019] Compound (A) can be any aldehyde capable of condensing at the ortho- and/or para- positions with respect to a hydroxyl present on an aromatic nucleus. Many aldehydes showed themselves suitable to this purpose. Preferably, formaldehyde, or its precursors, such as paraldehyde or paraformaldehyde, aliphatic aldehydes having from 2 to 5 10 carbon atoms, benzaldehyde or heterocyclic aldehydes such as, for example, furfural are used. A phenol compound (B) can be any mono- or polyhydroxylated phenol in which at least two of the ortho- and/or para-positions with respect to the hydroxy group or groups are free, for example, phenol, cresol, ethylphenol, resorcinol, pyrocatechol, hydroquinone, pyrogallol or bisphenol A, or a compound of formula (I):

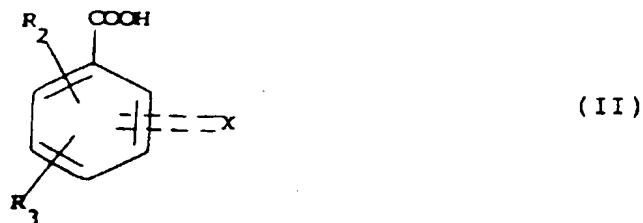
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wherein m is 1, 2 or 3, and R and R₁ are independently selected from the group consisting of hydrogen, halogen, (C₁₋₅) alkyl, hydroxy and carbo(C₁₋₅)alkoxy. Phenol, resorcinol or 1-naphthol are preferably used. Finally, compound (C) is preferably a hydroxylated aromatic carboxylic acid of formula II:

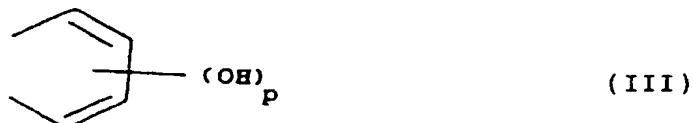
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wherein R₂ is selected from the group consisting of hydrogen, hydroxy, (C₁₋₅) alkoxy, (C₁₋₅) alkyl, hydroxy (C₁₋₅) alkyl, halogen, phenyl and hydroxyphenyl; R₃ has the same meanings of R₂ with the exclusion of hydrogen; x and the dotted lines, taken together, represent either a divalent residue ortho-condensed with the benzene ring of formula III:

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wherein p is an integer selected from 1 or 2, or they represent nothing; with the following provisos:

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- when x and the dotted lines, taken together, represent the residue of formula III, at least two of the ortho- and/or para- positions with respect to the hydroxyl group or groups must be free;
- when x and the dotted lines, taken together, represent nothing, at least one of R₂ or R₃ represent hydroxy, and at least two of the ortho- and/or para-positions with respect to the hydroxyl group or groups must be free.

[0020] Preferably, monohydroxy benzoic acids are used such as, for example, salicylic acid and 4-hydroxy-benzoic acid, dihydroxy benzoic acids such as, for example α -, β - and γ -resorcylic acids, 2,3-dihydroxy-benzoic acid, 2,5-dihydroxy-benzoic acid, monohydroxylated alkoxy benzoic acids such as, for example, 2-hydroxy-5-methoxybenzoic acid, hydroxy naphthoic acids such as, for example, 6-hydroxy-2-naphthoic acid.

5 [0021] The molar ratios of compounds (A), (B) and (C) as defined above can range within very wide limits, but this does not affect at all the excellent properties of the build-up suppressor agents of the present invention. Preferably, the molar ratios of aldehyde (A), phenol compound (B) and aromatic carboxylic acid hydroxy-substituted on the aromatic nucleus (C) are comprised, respectively, between 0.6 - 1.2 : 0.05 - 0.95 : 0.95 - 0.05. Still more preferably, the aldehyde is used in a molar amount not exceeding the sum of the moles of the compounds (B) and (C).

10 [0022] The build-up suppressor agents of the present invention can be prepared according to different procedures. In a first embodiment, the agents are obtainable reacting the compounds (A), (B) and (C) in aqueous solution in the above molar ratios, in the presence of a strong basic agent such as, for example, sodium or potassium hydroxide, so as to carry out the reaction at a pH ranging from 8 to 13.5. The compounds (A), (B), and (C) can be loaded together in the reaction vessel; alternatively a basic solution of the compounds (B) and (C) is prepared firstly and, after having heated at the temperatures indicated below, the component (A) is added. The temperature at which the reaction is carried out is, normally, between 40 and 120°C, and, preferably, between 70 and 100°C. The reaction times are not critical and can be advantageously comprised between 1 and 8 hours.

15 [0023] Alternatively, an aqueous basic solution (pH between 8 and 13.5), of compound (B) or of compound (C) is added to, or with an aqueous solution of compound (A), at a temperature comprised between 5 and 30°C. After having stirred for 1 - 3 hours at room temperature, an aqueous basic solution (pH as above reported) respectively of compound (C) or of compound (B) is added to the so obtained dimethylol compound and the resulting mixture is warmed to the temperature and for the times above described. These reactions can also be carried out *in situ*, namely on the reactor walls or, more in general, on any other part of reaction system which can be in contact with vinyl chloride or acetate, their mixtures or other monomers or polymers polymerizable with them, also in the form of vapours.

20 [0024] The methods for preparing the build-up suppressor agents of the invention and the build-up suppressor agents so obtained are a further object of the invention. These agents are polycondensed substances among the compounds (A), (B), and (C); they have a not too high molecular weight, and their structure is not well definable.

25 [0025] To the purpose of favouring the adhesion of the build-up suppressor agents of the present invention to those parts of the reaction system wherein it is desired that such adhesion occur, suitable surfactants or film forming agents such as, for example, polyvinyl alcohols with a high content of hydroxyls can be used.

30 [0026] Polyvinyl alcohols having a hydrolysis degree not lower than 96%, and a 4% water viscosity of 20 mPa.s or more, preferably 40 mPa.s or more, measured with a Hoppler viscosimeter, are preferred.

35 [0027] If used, these surfactants or film forming agents are mixed together with the obtained build-up suppressor agents in amounts ranging from about 2 and about 20% by weight, calculated on the build-up suppressor agents.

40 [0028] Other than those already cited, another advantage of the build-up suppressor agents of the invention lies in the fact that they can be obtained in solid form, are easy to handle and easily preservable. Therefore, at the moment of their application on the walls of the polymerization reactor, or of those other parts of the reaction system wherein the adhesion is desired, one can use one or more of the agents as such, as obtainable by the methods above described, or one or more of the agents recovered in the solid state and prepare with them a suitable composition.

45 [0029] Preferably, this composition is in liquid form, and can be prepared by dissolving one or more of the build-up suppressor agents of the invention in water and a basic agent, at a pH ranging from about 8 to about 13.5, or in a suitable organic solvent, optionally in the presence of the surfactants and film forming agents above mentioned.

50 [0030] The concentration of the build-up suppressor agents in the compositions for use in the application on the reactor walls or, more in general, of reaction system, is comprised between 0.2 and 15%, preferably between 0.4 and 9% calculated on the weight of the solution.

55 [0031] The quantity of the build-up suppressor agent of the present invention which must be applied on the walls of the reactors is particularly low, not more than 5 g of active substance per m² of surface and up to not less than 0.02 g per m² of surface, preferably up to not more than 3 g per m² and up to not less than 0.1 g per m² of surface.

[0032] In the case of liquid aqueous compositions, the build-up suppressor agent, after having been dissolved by means of a basic agent, such as for example sodium hydroxide or potassium hydroxide, or also by means of ammonia or lower aliphatic amines or mono- or triethanolamine, is generally applied by means of the well known water vapour- or pressurized nitrogen-spraying technique, but it can also be applied by brushing or, in the case of vinyl chloride, using the same monomer as carrier. The application can be carried out on cold or hot walls, using solutions previously heated or at room temperature, although the temperature is not critical. It can be also convenient to heat the inner walls of the reaction system after the application of the build-up suppressor agent.

[0033] The vinyl chloride or acetate polymerization dealt with in the present invention is either a homopolymerization or a copolymerization among them, in the presence or absence of one or more monomers or polymers polymerizable with them, such as for example other vinyl esters or aryl, alkyl or cycloalkyl esters of unsaturated mono- and polycar-

5 boxylic acids having 3-15 carbon atoms such as methyl acrylate, butyl methacrylate, acrylonitrile, the methacrylonitrile, unsaturated diesters, such as the diethyl maleate, allyl esters, such as allyl acetate, α -olefins, such as ethylene and propylene, vinyl ethers and styrene compounds. Moreover, the copolymerizations comprise also the polymerization of vinyl chloride in the presence of preformed polymers, optionally in the presence of grafting agents, to form grafted vinyl chloride polymers. Examples of these preformed polymers suitable for forming grafted vinyl chloride polymers comprise poly-2-ethylhexyl-acrylate, poly-n-butyl-acrylate and olefins/vinyl esters copolymers, such as ethylene/vinyl acetate copolymers.

10 [0034] The build-up suppressor agents of the present invention showed to be particularly effective in the case of aqueous suspension or aqueous emulsion polymerization, but also in the case of bulk polymerization a remarkable reduction of scales adhering to the walls is observed.

15 [0035] In the vinyl acetate and/or chloride suspension homo- and copolymerization suspending agents having colloid-protective properties can also be used, such as for example partially hydrolyzed polyvinyl acetates, cellulose ethers, gelatin, sorbitol esters of fatty acids.

20 [0036] The used amounts generally vary between 0.05 and 2% by weight calculated on the total of the used monomers.

25 [0037] In the emulsion polymerization, surfactants agents, such as polyglycol ethers of nonylphenol or sodium or ammonium salts of C₁₂-C₁₈ fatty acids, of alkylphosphates, of alkylsulfosuccinates, of alkylbenzene sulfonates, of sulfonated olefins, of sulfuric esters of fatty alcohols are used as emulsifiers agents.

30 [0038] The used amounts generally vary between 0.05 and 5% by weight calculated on the total of the used monomers.

35 [0039] Any suitable polymerization initiator, which is soluble in the used vinyl monomers can be employed. Examples of these catalysts, in the polymerization, are peroxides such as lauroyl peroxide, acetylcylohexylsulfonyl peroxide, azo compounds, such as azobis(dimethylvaleronitrile) and peroxidicarbonates such as dicetyl peroxidicarbonate, di-isopropyl peroxidicarbonate, bis-(4-tert-butyl-cyclohexyl)-peroxidicarbonate and the like. These initiators and any other conventional agent can be used in the usual amounts of 0.01 - 1% w/w on the total of the monomers used. In the emulsion polymerization oil-soluble initiators can be used, such as diaryl or dialkyl peroxides such as lauroyl or benzoyl peroxide, peresters such as t-butyl peroxyipivalate or t-butyl per-2-ethylhexanoate, peroxidicarbonate or dicetyl peroxidicarbonate or hydrosoluble redox initiator systems based on persulfates, hydrogen peroxide, hydroperoxides combined with sodium metabisulfite, sodium formaldehyde sulfoxilate and the like.

40 [0040] The operating conditions for the polymerization are those well known in the art and usually employed for emulsion, suspension and bulk polymerization of vinyl acetate and chloride, or of their mixtures, in the presence or absence of one or more monomers or polymers polymerizable with them.

45 [0041] The temperatures are in the range between 40 and 80°C and the pressure is generally comprised between 5 and 14 bar for vinyl chloride, and between 65 and 95°C and atmospheric pressure for vinyl acetate.

50 [0042] The following examples further illustrate the invention.

EXAMPLE 1

Preparation of a build-up suppressor agent

40 [0043] In a 2 liter glass reactor, equipped with stirrer, thermometer and bubble reflux condenser, 670 ml of water, 77 g (0.5 moles) of 3,5-dihydroxy-benzoic acid [(α -resorcylic acid), compound (C)], and 72 g (0.5 moles) of 1-naphthol [compound (B)] were loaded. The obtained suspension was added with 62 g (1.55 moles) of NaOH pellets and stirring was continued up to complete dissolution. Then, 90 g of a 30% formaldehyde [compound (A), 27 g, 0.9 moles] aqueous solution were slowly added, while continuously stirring, keeping the temperature below 50°C. Once the addition was finished, temperature was brought to 85°C and reaction mixture was kept at this temperature, under stirring, for about 3 hours. An aqueous solution of the build-up suppressor agent at a weight concentration of 20% was obtained.

45 [0044] This solution, after optional cooling at room temperature, can be brought to the desired concentration for the intended use as described before. If desired suitable surfactants or film forming agents may be added. Alternatively, by acidifying, filtering and drying the build-up suppressor agent in the solid state can be obtained.

EXAMPLES 2 - 7

50 [0045] Operating according to the procedure described in the preceding Example, build-up suppressor agents were prepared starting from the same compounds (A),(B), and (C) in molar ratios indicated below.

EX.	Compound(C) (moles)	Compound(B) (moles)	Compound(A) (moles)
2	0,1	0,9	0,9
3	0,05	0,95	0,9
4	0,95	0,05	0,9
5	0,25	0,75	0,9
6	0,5	0,5	0,8
7	0,75	0,25	1

EXAMPLE 8**Preparation of a build-up suppressor agent**

[0046] The procedure of the Example 1 was repeated starting from 0.1. moles of 2,4-dihydroxy-benzoic acid (C), 0.9 moles of 1-naphthol (B) and 0.9 moles of formaldehyde (A).

EXAMPLES 9 - 18

[0047] Build-up suppressor agents were prepared operating according to the methods described in the preceding Examples, starting from the compounds (A),(B) and (C) reported below. The molar ratios of the three components are also indicated.

EX.	(C): acid-	(B)	(A)	(C):(B):(A)
9	2,3-dihydroxy-benzoic	1-naphthol	formaldehyde	0,5:0,5:0,9
10	3,5-dihydroxy-benzoic	1-naphthol	acetaldehyde	0,75:0,25:0,9
11	3,5-dihydroxy-benzoic	phenol	formaldehyde	0,1:0,9:1
12	3,5-dihydroxy-benzoic	hydroquinone	formaldehyde	0,4:0,6:0,9
13	2,6-dihydroxy-benzoic	1-naphthol	formaldehyde	0,5:0,5:0,9
14	3,5-dihydroxy-benzoic	o-cresol	formaldehyde	0,3:0,7:1
15	6-hydroxy-2-naphthoic	phenol	formaldehyde	0,95:0,05:1
16	6-hydroxy-2-naphthoic	resorcinol	formaldehyde	0,95:0,05:0,9
17	3,5-dihydroxy-benzoic	1,3-dihydroxynaphthalene	formaldehyde	0,8:0,2:1
18	3,5-dihydroxy-benzoic	1,7-dihydroxynaphthalene	formaldehyde	0,1:0,9:0,9

EXAMPLE 19**Preparation of a build-up suppressor agent**

[0048] In a 2 liter-glass reactor, equipped with a stirrer, thermometer and bubble reflux condenser, 660 ml of water, 13.8 g (0.1 moles) of 2-hydroxy-benzoic acid [salicylic acid, compound (C)], 129.6 g (0.9 moles) of 1-naphthol [compound (B)] were loaded. The solution was added with 32 g (0.8 moles) of NaOH pellets and stirred up to complete dissolution. 90 g of a 30% formaldehyde aqueous solution [compound (A), 27 g, 0.9 moles] were then slowly added, while stirring, keeping the temperature below 50°C. At the end of the addition, the reaction mixture was warmed to 95°C and kept at this temperature, under stirring, for about 8 hours.

[0049] An aqueous solution of the build-up suppressor agent at a concentration by weight of 20% was obtained.

[0050] This solution, after optional cooling at room temperature, can be brought to the desired concentration for the intended use as described above. If desired, suitable surfactants or film forming agents may be added. Alternatively, by acidifying, filtering and drying the build-up suppressor agent in the solid state can be obtained.

EXAMPLES 20 - 23Preparation of a build-up suppressor agent

5 [0051] Operating according to the methods described in the preceding Example, build-up suppressor agents were prepared starting from the compounds (A),(B) and (C) reported below. The molar ratios of the three components are also indicated.

EX.	(C): acid :	(B)	(A)	(C):(B):(A)
20	4-hydroxy-benzoic	1-naphthol	formaldehyde	0,1:0,9:1
21	2-hydroxy-benzoic	1-naphthol	formaldehyde	0,5:0,5:0,7
22	2-hydroxy-benzoic	1-naphthol	formaldehyde	0,75:0,25:0,9
23	2-hydroxy-benzoic	1-naphthol	acetaldehyde	0,25:0,75:0,9

EXAMPLE 24Preparation of a build-up suppressor agent

20 [0052] 40 g (0.4 moles) of 30% formaldehyde were slowly added, at a temperature ranging between 10 and 20°C, with 30.8 g (0.2 moles) of 3,5-dihydroxy-benzoic acid [α -resorcylic acid, compound (C)] dissolved in 100 g of 9% NaOH. Once the addition was terminated, the mixture was stirred for 2 hours between 20 and 25°C, then 36 g (0.25 moles) of 1-naphthol dissolved in 220 g of 6.4% NaOH were added. The reaction mixture temperature was raised at 85 - 90°C and stirring at this temperature was continued for 3 hours. An aqueous solution of the build-up suppressor agent at a 20% weight concentration was obtained.

25 [0053] This solution, after optional cooling at room temperature, can be brought to the desired concentration for the intended use as described above. If desired, suitable surfactants or film forming agents may be added. Alternatively, by acidifying, filtering and drying the build-up suppressor agent in the solid state can be obtained.

EXAMPLE 25Preparation of a build-up suppressor agent

35 [0054] 82 g (0.82 moles) of 30% formaldehyde were slowly added, at a temperature below 30°C, to 61 g (0.4 moles) of 2,4-dihydroxybenzoic acid [β -resorcylic acid, compound (C)] dissolved in 476 g of 11% NaOH. Once the addition was terminated, the mixture was stirred for about 30 minutes between 20 and 30°C, then 72 g (0.5 moles) of 1-naphthol and 400 g of water were added. The reaction mixture was heated at 85°C and stirred at this temperature for 4 hours. An aqueous solution of the build-up suppressor agent at a 16% weight concentration was obtained.

40 [0055] This solution, after optional cooling at room temperature, can be brought to the desired concentration for the intended use as described above. If desired, suitable surfactants or film forming agents may be added. Alternatively, by acidifying, filtering and drying, the build-up suppressor agent in the solid state can be obtained.

EXAMPLES 26-29

45 [0056] Operating according to the procedures described in Examples 24 and 25, the following build up suppressor agents were prepared starting from the compounds (A), (B) and (C) reported below. The molar ratios of the three compounds are also indicated.

EX.	(C): benzoic acid:	(B)	(A)	(C):(B):(A)
26	2,4-dihydroxy	1-naphthol	formaldehyde	0.5 : 0.4 : 0.85
27	2,4-dihydroxy	1-naphthol	formaldehyde	0.6:0.4:0.9
28	3,5-dihydroxy	1-naphthol	formaldehyde	0.35 : 0.65 : 0.9
29	3,5-dihydroxy	1-naphthol	formaldehyde	0.4 : 0.6 : 0.85

EXAMPLE 30Polymerization of vinyl acetate monomer (VAM) in aqueous suspension

5 [0057] In a 25 liter-stainless steel reactor, equipped with a reflux condenser and anchor stirrer, the following ingredients were loaded in parts by weight:

VAM	100
water	50
PVOH (26/88)	0.05
Acetaldehyde	0.4
Sodium acetate	0.01
Benzoyl peroxide	0.03

10 [0058] The mixture was refluxed at atmospheric pressure and the polymerization was carried out for 4 hours until a conversion not lower than 99% was reached.

15 [0059] According to this procedure single polymerizations were carried out in the presence and absence of the build-up suppressor agents of the present invention. The agents were applied in the amount of 0.3 g per m² of reactor surface. The amount of build-up was determined after emptying and washing the reactor, collecting and weighing it.

20 [0060] The obtained results are reported in the following Table 1, and are expressed in parts per million (ppm) with respect to loaded monomers.

TABLE 1

EX.	Coating Agent of Example	Application	Build up (ppm)
30A	none	—	11800
30B	1	spray	250
30C	2	spray	300
30D	3	spray	300
30E	5	spray	230
30F	7	spray	180
30G	10	spray	370
30H	14	spray	260
30I	16	vapour	80
30L	19	vapour	305
30M	20	vapour	200
30N	21	vapour	280

45 [0061] Similar results were obtained by applying the build-up suppressor agents of the Examples 1, 2, 3, 4, 7, 8, 19, 20 and 21 in the amount of 0.1 g of ingredient active per m² of reactor surface.

EXAMPLE 31Polymerization of vinyl chloride monomer (VCM) in aqueous suspension

50 [0062] In a 100 liter, internally glass lined, stainless steel reactor, equipped with a Pfaudler stirrer, after having eliminated oxygen, the following ingredients were loaded in parts by weight:

VCM	100
Water	150

(continued)

POLIVIC S 404 W™ (3V SIGMA, Italy)	0.04*
POLIVIC SP 808™ (3V SIGMA, Italy)	0.04*
Methylhydroxypropylcellulose	0.04
Sodium hydrogencarbonate	0.03
Bis(4-ter-butylcyclohexyl)peroxy dicarbonate	0.04

*as active substance

[0063] The system was heated to 54°C, corresponding to a K-value of PVC polymer of about 70, whereas the pressure raised at 7/8 ate, and the polymerization was carried out for about 7 hours. When the pressure was falling by 2-3 ate, the reaction was stopped exhausting the unreacted monomer and isolating it.

[0064] According to this procedure, single polymerizations were carried out in the presence and absence of the build-up suppressor agents of the present invention.

[0065] The build-up suppressor agents were applied in the amount of 0.5 g per m² of reactor surface. The amount of build-up was determined after emptying and washing the reactor, collecting and weighing it. The results obtained are reported in Table 2 below and are expressed in parts per million (ppm) with respect to the loaded monomer.

TABLE 2

EX.	Coating Agent of Example	Application	Build up (ppm)
31A	none	-----	6800
31B	1	spray	traces
31C	2	spray	25
31D	3	spray	25
31E	4	spray	10
31F	7	spray	30
31G	8	spray	15
31H	13	spray	traces
31I	19	spray	25
31L	20	spray	10
31M	21	spray	traces
31N	25	spray	absent
31O	27	spray	absent

[0066] The PVC obtained from Examples 31 B, D, F, H and N, were stabilized against the thermo-oxidative degradation with calcium and zinc stearate and were pressure-molded into plates having 1.5 mm thickness. The yellow index (YI) of the plates was measured with a reflection spectrophotometer obtaining the values reported in Table 3 below:

TABLE 3

Example	YI
31B	7.6
31D	7.6
31F	7
31H	7.4
31N	7.4

[0067] The polymers obtained according to the present invention showed better appearance.

EXAMPLE 32

[0068] The same polymerization of the preceding example was performed for four consecutive times, in the absence or presence of the build-up suppressor agents. When the latter were present, they were applied in the amount of 0.5 g per m² of reactor surface, only one time before the first polymerization. The amount of build-up was determined after emptying and washing the reactor at the end of the fourth loading, collecting and weighing it.

[0069] The results obtained are reported in the Table 4 and are expressed in parts per million (ppm) with respect to the amount of the loaded monomer.

TABLE 4

EX.	Coating Agent of Example	Application	Build up (ppm)
32A	none	-----	13000
32B	1	spray	15
32C	2	spray	60
32D	3	spray	65
32E	7	spray	70
32F	13	spray	20
32G	19	spray	45
32H	21	spray	20
32I	8	spray	traces
32L	25	spray	absent
32M	27	spray	traces
32N	28	spray	absent

[0070] The obtained PVCs were stabilized against the thermo-oxidative degradation with calcium and zinc stearate and were pressure-molded into plates having 1.5 mm thickness. The yellow index (YI) of the plates gave values superimposable to those of the preceding Example.

EXAMPLE 33**Copolymerization vinyl acetate monomer (VAM)/Vinyl esters in aqueous dispersion**

[0071] In a 25 liter-stainless steel reactor, equipped with reflux condenser and anchor stirrer, 30% of the monomer mixture and 50% of the Redox initiator system below described in parts by weight were loaded:

VAM	70
Dibutyl maleate	30
Water	70
Hydroxyethylcellulose (WP 300)	2
Ethoxylated nonyl-phenol	2.3
NaHCO ₃	0.07
tert-butylhydroperoxide	0.18
sodium formaldehyde sulfoxilate	0.089.

[0072] The mixture was refluxed at atmospheric pressure and the remaining material was loaded in 5 hours at the temperature of 85°C.

[0073] After completing the reaction, cooling and unloading the reactor, the latter was washed with water at 5 ate.

[0074] According to this procedure, single polymerizations in the presence and in absence of the build-up suppressor agents of the present invention were effected. The agents were applied in the amount of 0.3 g per m² of reactor surface. The amount of build-up was determined after emptying and washing the reactor, collecting and weighing it.

[0075] The results obtained are reported in the following Table 5, and are expressed in parts per million (ppm) with

respect to the loaded monomers.

TABLE 5

EX.	Coating Agent of Example	Application	Build up (ppm)
33A	none	-----	21000
33B	1	spray	traces
33C	2	spray	30
33D	5	spray	30
33E	16	spray	traces
33F	19	spray	25
33G	25	spray	traces

EXAMPLE 34

[0076] The same copolymerization of the preceding Example was repeated for 3 consecutive times, in the absence or in the presence of the build-up suppressor agents of the present invention. When operating in the presence of the latter, they were applied in the amount of 0.3 g per m² of reactor surface, a single time, before the first polymerization. The amount of build-up was determined after emptying and washing the reactor at the end of the third load, collecting and weighing it. The results obtained are reported in Table 6 and are expressed in parts per million (ppm) with respect to the amount of the loaded monomer.

TABLE 6

EX.	Coating Agent of Example	Application	Build up (ppm)
34A	none	-----	38000
34B	1	spray	30
34C	2	spray	70
34D	15	spray	75
34E	16	spray	25
34F	19	spray	60
34G	25	spray	traces

[0077] The copolymer obtained from Examples 34B, D, E and G was stabilized against the thermo-oxidative degradation with calcium and zinc stearate and were pressure-molded into plates having 1.5 mm thickness. The yellow index (YI) of the plates was measured with a reflection spectrophotometer obtaining the values reported in Table 7 below:

TABLE 7

Example	YI
34B	8.2
34D	8
34E	8.3
34G	8.4

[0078] The polymers obtained showed a better appearance.

EXAMPLE 35Polymerization of vinyl chloride monomer (VCM) in aqueous suspension

5 [0079] The inner walls of a stainless-steel polymerization reactor of 40 m³ capacity were coated by means of the steam spraying technique with an aqueous strong alkaline solution of the compound of Example 25, so as to provide an amount of build-up suppressant of 0,75 g/m². Subsequently, the following ingredients were loaded in parts by weight.

10	VCM	100
	Water	150
	POLIVIC(R)S 404 W (3V SIGMA, Italy)	0.05*
	GOHSENO(R)KH 17 (NIPPON GOHSEI, Japan)	0.055
	ALCOTEX(R)72.5 (REVERTEX, UK)	0.025
15	sodium hydrogencarbonate	0.03
	bis-(4-tert.-butylcyclohexyl)-peroxidicarbonate	0.03
	lauroyl peroxide	0.04

*as active substance

20 [0080] The system was heated to about 54°C, corresponding to a K value of the PVC polymer of about 70, with the pressure raising to 7-8 atmospheres, and the polymerization was carried on for about 6 hours. When the pressure fell down by 2-3 atmospheres, the reaction was stopped venting out and recovering the unreacted monomer.
 [0081] At least eighty consecutive polymerizations were carried out without cleaning the inner walls of the reactor before each run, but simply rinsing them with water and applying the build-up suppressant before each polymerization
 25 as above indicated. No build-up formation was observed.

EXAMPLE 36

30 [0082] The polymerization of the above Example was repeated in a stainless-steel reactor of 100 m³ equipped with a condenser, coating the inner walls of both the reactor and the condenser by the steam spraying technique with an aqueous strong alkaline solution of the compound of Example 1 so as to provide an amount of build-up suppressant of 0.63 g/m². Also in these plant-scale trials, at least eighty consecutive polymerizations were carried out without cleaning the inner walls of the reactor and the condenser before each run, but simply rinsing them with water and applying the build-up suppressant before each polymerization as above indicated. No build-up formation was observed.
 35 The same results were achieved by employing the build-up suppressants of Examples 25 and 27.

EXAMPLE 37

40 [0083] The inner walls of a stainless-steel polymerization reactor of 26 m³ capacity were coated by means of the nitrogen spraying technique with an aqueous strong alkaline solution of the compound of Example 25, previously diluted with water in a 1:10 (v:v) ratio, so as to provide an amount of build-up suppressant of 0.75 g/m². Once the spraying was terminated, the reactor walls were heated for 1 minute at about 60°C. Subsequently, the following ingredients
 45 were loaded in parts by weight.

50	VCM	100
	Water	150
	POLIVIC(R)S 404 W (3V SIGMA, Italy)	0.04*
	GOHSENO(R)KH 17 (NIPPON GOHSEI, Japan)	0.06
	bis-(4-tert.-butylcyclohexyl)-peroxidicarbonate	0.03
	lauroyl peroxide	0.04

*as active substance

55 [0084] The system was heated to about 59°C, corresponding to a K value of the PVC polymer of about 65, while the pressure raised to 8-10 atmospheres. The polymerization was carried on for about 5 hours. When the pressure de-

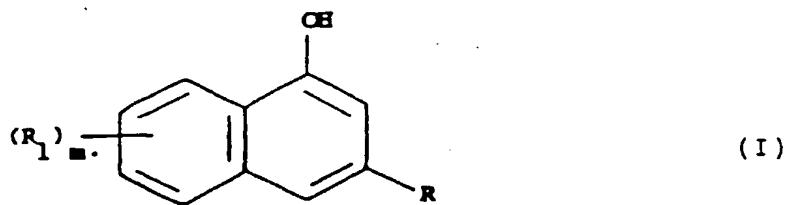
creased by 2-3 atmospheres, the reaction was stopped by venting out and recovering the unreacted monomer. At least eight consecutive polymerizations were carried out without applying the build-up suppressant before each run. No build-up formation was observed. The same results were achieved by employing the build-up suppressants of Examples 8 and 24.

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Claims

1. Build-up suppressor agents comprising condensation products between an aldehyde, a phenol compound and an aromatic carboxylic acid hydroxylated on the aromatic nucleus.
- 10 2. Build-up suppressor agents according to claim 1, characterized in that the aldehyde is an aldehyde capable of condensing at ortho- and/or para- positions with respect to a hydroxyl on the aromatic nucleus.
- 15 3. Build-up suppressor agents according to claim 1, characterized in that the phenol compound is a mono- or poly-hydroxylated phenol in which at least two of the ortho- and/or para- positions with respect to the hydroxy group or groups are free, or the phenol compound is a compound of formula (I):

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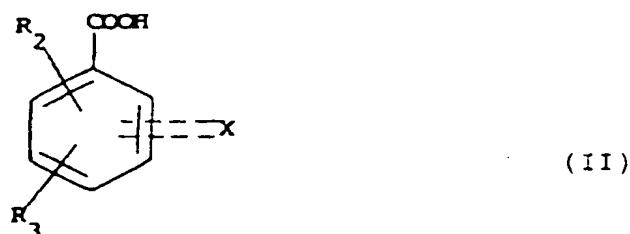
wherein m is 1, 2 or 3, and R and R₁ are independently selected from the group consisting of hydrogen, halogen, (C₁₋₅) alkyl, hydroxy and carbo(C₁₋₅)alkoxy.

30

4. Build-up suppressor agents according to claim 1, characterized in that the aromatic carboxylic acid hydroxylated on the aromatic nucleus is a compound of formula II

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wherein R₂ is selected from the group consisting of hydrogen, hydroxy, (C₁₋₅)alkoxy, (C₁₋₅)alkyl, hydroxy(C₁₋₅)alkyl, halogen, phenyl and hydroxyphenyl; R₃ has the same meanings of R₂, except hydrogen; x and the dotted lines, taken together, can represent either the bivalent radical ortho-condensed with benzene ring of formula III

55



wherein p is an integer selected from 1 or 2, or they represent nothing; .
with the following provisos:

5 a) when x and the dotted lines, taken together, represent the residue of formula III, at least two of the ortho- and/or para- positions with respect to the hydroxyl group or groups must be free;
b) when x and the dotted lines, taken together, represent nothing, at least one of R₂ or R₃ represent hydroxy, and at least two of the ortho- and/or para-positions with respect to the hydroxyl group or groups must be free.

10 5. Build up suppressor agents according to anyone of claims 1 to 4, in acidic form or in the form of the corresponding salts with basic agents.

15 6. A process for the preparation of a build-up suppressor agent according to anyone of claims 1 to 5, which comprises reacting the aldehyde, the phenol compound and the aromatic carboxylic acid hydroxylated on the aromatic nucleus in the presence of a strong alkali agent, at a temperature ranging from 40 to 120°C, for a period of time ranging from 1 and 8 hours.

20 7. A process according to claim 6, characterized in that the aldehyde, the phenol compound and the aromatic carboxylic acid hydroxylated on the aromatic nucleus are reacted in molar ratios ranging, respectively, from 0.6-1.2: 0.05-0.95:0.95-0.05.

25 8. A process according to claims 6 and 7, characterized in that firstly the aldehyde is reacted with the phenol compound or, in alternative, with the aromatic carboxylic acid hydroxylated on the aromatic nucleus, and the so obtained dimethylol compound is subsequently reacted with the carboxylic acid hydroxylated on the aromatic nucleus or with the phenol compound, respectively.

30 9. Build-up suppressor agents according to anyone of claims from 1 to 5 obtainable according to the process of claims 6 to 8.

35 10. A composition having anti build-up activity containing one or more of the build-up suppressor agents according to anyone of claims 1, 2, 3, 4, 5 or 9 and a suitable vehicle.

40 11. A composition according to claim 10, wherein the vehicle is a liquid.

45 12. The use of one or more of the build-up suppressor agents according to anyone of claims 1, 2, 3, 4, 5 or 9 in a vinyl chloride or vinyl acetate polymerization process, or of mixtures thereof, in the presence or absence of other monomers or polymers polymerizable with them.

50 13. A method for suppressing the formation of build-up in the polymerization processes of vinyl chloride or vinyl acetate, or of their mixtures, in the presence or in absence of other monomers or polymers polymerizable with them, which comprises coating the inner walls of a polymerization reactor with one or more of the build-up suppressor agents according to anyone of claims 1, 2, 3, 4, 5 or 9.

55 14. A process for the polymerization of vinyl chloride or of vinyl acetate, or of mixtures thereof, in the presence or absence of other monomers or polymers polymerizable with them, carried out in a reactor whose inner walls are coated with one or more of the build-up suppressor agents according to anyone of claims 1, 2, 3, 4, 5 or 9.

60 15. A polymerization reactor whose inner walls are coated with one or more of the build-up suppressor agents according to anyone of claims 1, 2, 3, 4, 5 or 9.

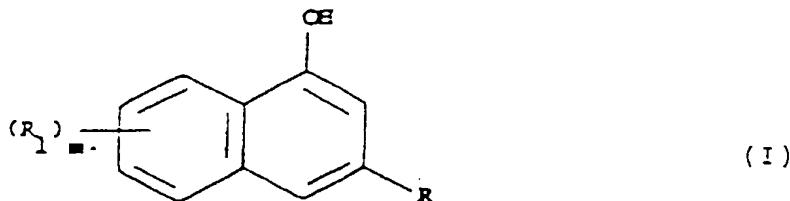
50 **Patentansprüche**

1. Mittel zur Unterdrückung von Belagbildung, umfassend Kondensationsprodukte zwischen einem Aldehyd, einer Phenolverbindung und einer aromatischen Carbonsäure, die am aromatischen Kern hydroxyliert ist.

55 2. Mittel zur Verhinderung von Belagbildung nach Anspruch 1, dadurch charakterisiert, dass der Aldehyd eine Aldehyd ist, der zur Kondensation an den ortho- und/oder para-Positionen bezogen auf ein Hydroxyl am aromatischen Kern fähig ist.

3. Mittel zur Verhinderung von Belagbildung nach Anspruch 1, dadurch charakterisiert, dass die Phenolverbindung ein mono- oder polyhydroxyliertes Phenol ist, bei dem mindestens zwei der ortho- und/oder para-Positionen bezogen auf die Hydroxygruppe oder -gruppen frei sind, oder dass die Phenolverbindung eine Verbindung der Formel (I) ist:

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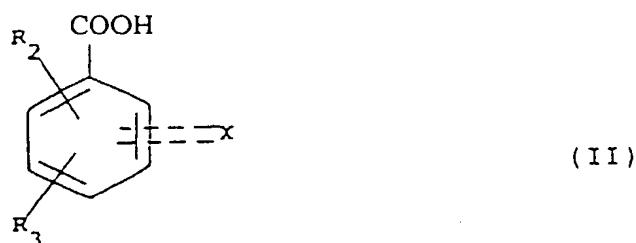


wobei m 1, 2 oder 3 ist, und R und R₁ unabhängig voneinander ausgewählt werden aus der aus Wasserstoff, Halogen, (C₁₋₅)Alkyl, Hydroxy und Carbo (C₁₋₅) alkoxy bestehenden Gruppe.

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4. Mittel zur Unterdrückung von Belagbildung nach Anspruch 1, dadurch charakterisiert, dass die am aromatischen Kern hydroxylierte aromatische Carbonsäure eine Verbindung der Formel II ist

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wobei R₂ ausgewählt wird aus der aus Wasserstoff, Hydroxy, (C₁₋₅) Alkoxy, (C₁₋₅) Alkyl, Hydroxy (C₁₋₅) alkyl, Halogen, Phenyl und Hydroxyphenyl bestehenden Gruppe; R³ dieselbe Bedeutung hat wie R², mit Ausnahme von Wasserstoff; x und die gestrichelten Linien zusammengenommen entweder den mit dem Benzolring ortho-kondensierten bivalenten Rest der Formel III

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wobei p eine aus 1 oder 2 ausgewählte ganze Zahl ist, darstellen können, oder sie nichts darstellen; mit den folgenden Maßgaben:

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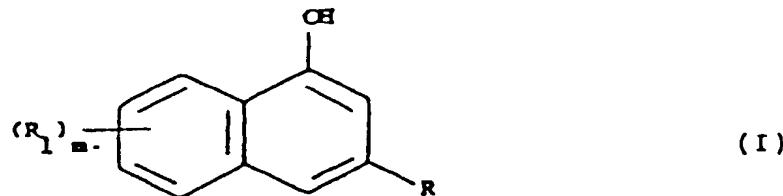
- a) wenn x und die gestrichelten Linien zusammengenommen den Rest der Formel III darstellen, müssen mindestens zwei der ortho- und/oder para-Positionen bezogen auf die Hydroxylgruppe oder -gruppen frei sein,
- b) wenn x und die gestrichelten Linien zusammengenommen nichts darstellen, stellt mindestens einer von R₂ oder R₃ Hydroxy dar, und mindestens zwei der ortho- und/oder para-Positionen bezogen auf die Hydroxylgruppe oder -gruppen müssen frei sein.

5. Mittel zur Unterdrückung von Belagbildung nach einem der Ansprüche 1 bis 4, in saurer Form oder in Form der entsprechenden Salze mit basischen Mitteln.
6. Verfahren zur Herstellung eines Mittels zur Verhinderung von Belagbildung nach einem der Ansprüche 1 bis 5, welches Umsetzen des Aldehyds, der Phenolverbindung und der am aromatischen Kern hydroxylierten aromatischen Carbonsäure in Gegenwart eines stark alkalischen Mittels, bei einer Temperatur im Bereich von 40 bis 120°C, während einer Zeit von 1 bis 8 Stunden umfasst.
10. Verfahren nach Anspruch 6, dadurch charakterisiert, dass der Aldehyd, die Phenolverbindung und die am aromatischen Kern hydroxylierte aromatische Carbonsäure in molaren Verhältnissen von jeweils 0.6-1.2:0.05-0.95: 0.95-0.5 umgesetzt werden.
15. Verfahren nach den Ansprüchen 6 und 7, dadurch charakterisiert, dass der Aldehyd zunächst mit der Phenolverbindung umgesetzt wird oder alternativ mit der am aromatischen Kern hydroxylierten aromatischen Carbonsäure, und die so erhaltene Dimethylolverbindung anschließend mit der am aromatischen Kern hydroxylierten Carbonsäure beziehungsweise mit der Phenolverbindung umgesetzt wird.
20. Mittel zur Verhinderung von Belagbildung nach einem der Ansprüche 1 bis 5, erhältlich nach dem Verfahren der Ansprüche 6 bis 8.
25. Zusammensetzung mit einer Aktivität zur Verhinderung von Belagbildung, enthaltend eines oder mehrere der Mittel zur Unterdrückung von Belagbildung nach einem der Ansprüche 1, 2, 3, 4, 5 oder 9 und einen geeigneten Träger.
11. Zusammensetzung nach Anspruch 10, wobei der Träger eine Flüssigkeit ist.
25. Verwendung von einem oder mehreren der Mittel zur Verhinderung von Belagbildung nach einem der Ansprüche 1, 2, 3, 4, 5 oder 9 in einem Vinylchlorid- oder Vinylacetat-Polymerisationsverfahren, oder von Gemischen davon, in Gegenwart oder Abwesenheit von weiteren Monomeren oder Polymeren, die mit ihnen polymerisierbar sind.
30. 13. Verfahren zur Unterdrückung der Bildung von Belägen in Polymerisationsverfahren von Vinylchlorid oder Vinylacetat oder von deren Gemischen in Gegenwart oder Abwesenheit von anderen Monomeren oder Polymeren, die mit ihnen polymerisierbar sind, welches Beschichten der Innenwände eines der Polymerisationsreaktors mit einem oder mehreren der Mittel zur Verhinderung von Belagbildung nach einem der Ansprüche 1, 2, 3, 4, 5 oder 9 umfasst.
35. 14. Verfahren zur Polymerisation von Vinylchlorid oder Vinylacetat oder von Gemischen davon in Gegenwart oder Abwesenheit von anderen Monomeren oder Polymeren, die mit ihnen polymerisierbar sind, durchgeführt in einem Reaktor, dessen Innenwände mit einem oder mehreren der Mittel zur Verhinderung von Belagbildung nach einem der Ansprüche 1, 2, 3, 4, 5 oder 9 beschichtet sind.
40. 15. Polymerisationsreaktor, dessen Innenwände mit einem oder mehreren der Mittel zur Verhinderung von Belagbildung nach einem der Ansprüche 1, 2, 3, 4, 5 oder 9 beschichtet sind.

45. **Revendications**

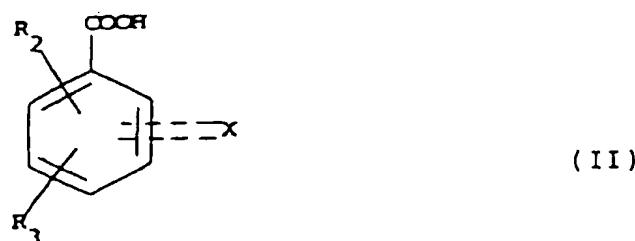
1. Agents suppresseurs de dépôt comprenant des produits de condensation entre un aldéhyde, un composé phénolique et un acide carboxylique aromatique hydroxylé sur le noyau aromatique.
50. 2. Agents suppresseurs de dépôt selon la revendication 1, caractérisés en ce que l'aldéhyde est un aldéhyde capable de condensation aux positions *ortho* et/ou *para* par rapport à un groupe hydroxyle sur le noyau aromatique.
3. Agents suppresseurs de dépôt selon la revendication 1, caractérisés en ce que le composé phénolique est un mono- ou polyphénol dans lequel au moins deux des positions *ortho* et/ou *para* par rapport au groupe ou aux groupes hydroxyle sont libres, ou bien le composé phénolique est un composé de formule (I):

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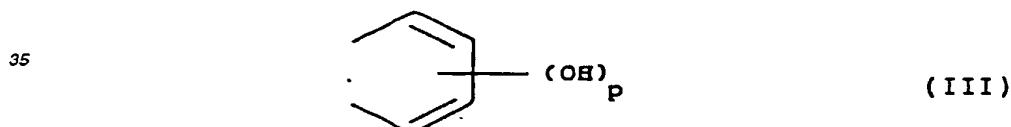


10 dans laquelle m est 1, 2 ou 3, et R et R₁ sont choisis indépendamment dans la classe formée par l'hydrogène, un halogène, les groupes alkyles en C₁-C₅, hydroxyle et carbo(alcoxy en C₁-C₅).

15 4. Agents suppresseurs de dépôt selon la revendication 1, caractérisés en ce que l'acide carboxylique aromatique hydroxylé sur le noyau aromatique est un composé de formule II



30 dans laquelle R₂ est choisi dans la classe formée par l'hydrogène, les groupes hydroxyle, alcoxy en C₁-C₅, alkyles en C₁-C₅, hydroxyalkyles en C₁-C₅, halogéno, phényle et hydroxyphényle ; R₃ a la même définition que R₂, à l'exception de l'hydrogène ; x et les lignes en traits interrompus, considérés ensemble, peuvent représenter le radical divalent condensé en *ortho* avec le noyau benzénique de formule III



40 où p est un nombre entier choisi parmi 1 ou 2, ou bien ne représentent rien ; avec les conditions suivantes :

45 a) si x et les lignes en traits interrompus, considérés ensemble, représentent le résidu de formule III, au moins deux des positions *ortho* et/ou *para* par rapport au groupe ou aux groupes hydroxyle doivent être libres ; b) si x et les lignes en traits interrompus, considérés ensemble, ne représentent rien, au moins l'un de R₂ ou R₃ représente un groupe hydroxyle, et au moins deux des positions *ortho* et/ou *para* par rapport au groupe ou aux groupes hydroxyle doivent être libres.

50 5. Agents suppresseurs de dépôt selon l'une quelconque des revendications 1 à 4, sous forme acide ou sous la forme des sels correspondants avec des agents basiques.

55 6. Un procédé pour la préparation d'un agent suppresseur de dépôt selon l'une quelconque des revendications 1 à 5, qui consiste à faire réagir l'aldéhyde, le composé phénolique et l'acide carboxylique aromatique hydroxylé sur le noyau aromatique en présence d'un agent alcalin fort à une température comprise dans l'intervalle de 40 à 120°C, pendant une période de temps comprise entre 1 et 8 heures.

7. Un procédé selon la revendication 6, caractérisé en ce que l'aldéhyde, le composé phénolique et l'acide carboxy-

lique aromatique hydroxylé sur le noyau aromatique sont amenés à réagir en des rapports molaires s'établissant respectivement de 0,6 à 1,2; 0,05 à 0,95; 0,95 à 0,05.

- 5 8. Un procédé selon les revendications 6 et 7, caractérisé en ce que l'aldéhyde est d'abord amené à réagir avec le composé phénolique ou, en variante, avec l'acide carboxylique aromatique hydroxylé sur le noyau aromatique, et le composé diméthylolé ainsi obtenu est ensuite amené à réagir avec l'acide carboxylique hydroxylé sur le noyau aromatique ou avec le composé phénolique, respectivement.
- 10 9. Agents suppresseurs de dépôt selon l'une quelconque des revendications 1 à 5, pouvant être obtenus selon le procédé des revendications 6 à 8.
- 15 10. Une composition ayant une activité anti-dépôt, contenant un ou plusieurs des agents suppresseurs de dépôt selon l'une quelconque des revendications 1, 2, 3, 4, 5 ou 9, et un véhicule approprié.
- 20 11. Une composition selon la revendication 10, dans laquelle le véhicule est un liquide.
- 25 12. L'utilisation d'un ou plusieurs des agents suppresseurs de dépôt selon l'une quelconque des revendications 1, 2, 3, 4, 5 ou 9 dans un procédé de polymérisation de chlorure de vinyle ou d'acétate de vinyle, ou de mélanges de ceux-ci, en la présence ou l'absence d'autres monomères ou polymères polymérisables avec eux.
- 30 13. Un procédé pour supprimer la formation de dépôt dans les procédés de polymérisation de chlorure de vinyle ou d'acétate de vinyle, ou de mélanges de ceux-ci, en la présence ou l'absence d'autres monomères ou polymères polymérisables avec eux, qui consiste à enduire les parois internes d'un réacteur de polymérisation avec un ou plusieurs des agents suppresseurs de dépôt selon l'une quelconque des revendications 1, 2, 3, 4, 5 ou 9.
- 35 14. Un procédé pour la polymérisation de chlorure de vinyle ou d'acétate de vinyle, ou de mélanges de ceux-ci, en la présence ou l'absence d'autres monomères ou polymères polymérisables avec eux, exécuté dans un réacteur dont les parois internes sont enduites d'un ou plusieurs des agents suppresseurs de dépôt selon l'une quelconque des revendications 1, 2, 3, 4, 5 ou 9.
- 40 15. Un réacteur de polymérisation dont les parois internes sont enduites d'un ou plusieurs des agents suppresseurs de dépôt selon l'une quelconque des revendications 1, 2, 3, 4, 5 ou 9.

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